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Sodium borohydride as a fuel for the future

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ABSTRACT

In a time of unprecedented change in environmental, geopolitical and socio-economic world affairs, the search for new energy materials has become a topic of great relevance. Sodium borohydride, $NaBH_4$, seems to be a promising fuel in the context of the future hydrogen economy. $NaBH_4$ belongs to a class of materials with the highest gravimetric hydrogen densities, which has been discovered in the 1940s by Schlesinger and Brown. In the present paper, the most relevant issues concerning the use of $NaBH_4$ are examined. Its basic properties are summarised and its synthesis methods are described. The general processes of $NaBH_4$ oxidation, hydrolysis, and monitoring are reviewed. A comprehensive bibliometric analysis of the $NaBH_4$ publications in the energy field opens the discussion for current perspectives and future outlook of $NaBH_4$ as an efficient energy/hydrogen carrier. Despite the observed exponential increase in the research on $NaBH_4$ it is clear that further efforts are still necessary for achieving significant overchanges.

Contents

1. The overall energy scene

The mastery of energy has always been the key to a better world. Energy can be defined as an abstract quantity that manifests itself in many forms, *e.g.*, chemical, electrical, mechanical, radiant, nuclear, and thermal energy. In an electric vehicle, for example, a battery is used to convert chemical energy into electrical energy, which is then converted to mechanical energy by a motor. The scientific use of the term "energy" was introduced by Thomas Young (1773–1829) who provided the most astute definition to date, as "energy is the ability to do work". It is commonly understood that "work" means the application of effort to accomplish a task, and the rate at which work is performed is called "power". Thus, machines consume energy, perform work, and provide power [1].

Until the advent of the Industrial Revolution in the 18th century, humankind derived its power mainly from its own exertions, from animal muscle (horses, oxen, camels), from the wind (windmills and sailing ships), and from water (watermills). Even with these

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limited resources, however, some humankind's achievements were remarkable.

Sources of power began to change with the development of the "atmospheric" engine in the early 18th century by Thomas Newcomen (1663–1729), who was inspired by the earlier work of Denis Papin (1647–1712) and Thomas Savery (1650–1716).

James Watt (1736–1819) subsequently recognised that the "atmospheric" engine was very inefficient – energy was wasted by having to reheat the cylinder after each stroke of the piston. Watt solved this problem using a separate condenser and driving the engine by the pressure of steam itself. Thus, in 1769, he patented the first real "steam" engine, which offered superior performance in terms of both energy efficiency and economy. By the early 19th century, steam was also replacing water to power cotton mills and *The Times* newspaper was printed in London on a steam press as early as 1814. Thus, such engines turned steam into a universal source of power and heralded the beginning of the fossil-fuel age. By the end of the 19th century, there were steam-driven cars in London, Paris and New York as well as lorries and trams. These competed with electric vehicles and petrol-driven vehicles. Eventually, the internal-combustion engine proved superior, and steam vehicles were mostly phased out, although their use in agriculture continued for at least another 20 years.

Coal was the first fossil fuel to be exploited to produce power. In the 19th century, the pyrolysis of coal yielded coal gas ("town gas"), which was distributed in cities for lighting lamps and cooking, and coal tar, which was the early raw material for the organic chemicals industry (explosives, dyes, drugs, etc.). As recently as 1937, coal accounted for three-quarters of energy consumption worldwide through its use as a fuel for space heating, cooking, industrial processes, and transportation (steam trains and ships) [1].

In 1876, the four-stroke internal-combustion engine was built by the German engineer, Nikolaus Otto (1832–1891), initiating the petroleum ("oil") industry. Otto's engines ran at slow speed and it was not until 1885 that a suitable power unit for motor cars (automobiles) became available – the high-speed engine invented by Gottlieb Daimler (1834–1900). Shortly afterwards, in 1892, Rudolf Diesel (1858–1913) introduced the diesel engine. The success of internal-combustion engines operating on petroleum ("gasoline") was such that they rapidly replaced the steam engine (an external combustion engine) for almost all other applications although, of course, steam turbines are still used in electricity generation.

Just how far the motor car has come in a little more than 100 years is quite remarkable, although on the pollution front we have merely replaced one environmental problem (horse manure) with another (tailpipe emissions). The 20th century saw the widespread adoption of the internal-combustion engine for transport and power applications. The use of this engine has become so extensive that a serious concern has arisen over the pollution it causes in cities, and also over its contribution to global warming through enhancement of the "greenhouse effect", which is attributable in part to the carbon dioxide (CO_2) produced by combustion [1].

Another major change that took place towards the end of the 19th century was the growth of the electrical industry, initiated by the earlier research of Michael Faraday (1791–1867) on electromagnetic induction.

During the second half of the 20th century, there has been wholesale exploitation of natural gas – the third major fossil fuel. Over the past decade or so, there has been a marked swing towards the combustion of gas for the centralised generation of electricity. This may be explained by the abundance, accessibility and relatively low cost of natural gas, its convenience of transport and use, and the high efficiency of the combined-cycle gas turbine.

Energy from the three great fossil fuels – coal, petroleum and natural gas – has provided the means by which our industry and our civilisation have steadily progressed since the Industrial Revolution. In the long term, this is obviously an unsustainable situation as fossil fuels are being extracted at a rate that grossly exceeds the rate at which they are laid down. Moreover, the atmosphere will no longer accept unlimited combustion of fossil fuels. Consequently, it will be necessary to move away from fossil fuels, towards sustainable energy supplies of a non-polluting nature, while maintaining the standard of living of the developed world and dramatically improving that of developing nations.

Fortunately, nature has bestowed upon us a bountiful supply of such benevolent energy, in the forms of hydro energy, wind energy, wave energy, tidal energy, ocean thermal energy, solar energy, geothermal energy, and biomass. The task, therefore, is to capture and utilise greater amounts of these renewable energies in an efficient and economical way so as to minimise the environmental impact of energy consumption by the industry, transportation, agriculture, commerce and domestic sectors.

The European "World Energy, Technology and Climate Policy Outlook (WETO)" predicted an average annual growth rate of 1.8% for the period from 2000 to 2030, for primary energy worldwide [2]. The International Energy Agency (IEA)'s forecast of the world demand for primary energy in 2010 [3] and 2020 [4] is shown in Table 1. Compared with the situation in 2001, the IEA predicted a 21% increase in 2010 (12,100 Mtoe) (1 Mtoe is 1 million tonne oil equivalent) and a 48% increase in 2020 (14,800 Mtoe) [5]. Fossil fuels (oil, coal, natural gas) will continue to provide about 80–85% of the world's primary energy right through 2020. Oil, in the form of petroleum, will be the dominant fuel and will meet 35–37% of global energy needs. This will require an increase in production from around 110 Mb d^{-1} in 2020 (Mb d^{-1} stands for million barrels per day; 1 tonne of crude oil approximates to 7.4 barrels). This reflects a substantial increase in the demand for transportation fuels. Shell company, for example, has predicted that oil consumption by road vehicles in 2020 will be 40% higher than today. But whether or not such increased production will take place is, in part, a political question. Nuclear power output will decline as a proportion of the total energy supply as older reactors in Europe and North America are retired. The apparent increase in "renewables", categorised under "Other" in Table 1, is misleading. If the estimated contribution from wood and dung in developing nations is deducted, the expected contribution from "new" renewable sources (geothermal, solar, wind, tidal, etc.) will increase from 0.5% to between 1% and 3% of the total primary energy supply [1].

Table 1
Primary energy supply by fuel (%) for world in 2001 and forecast for 2010 and 2020 [3,4].

	Year		
	2001	2010	2020
Oil	35.0	35.3	37.0
Coal	23.3	22.3[a]	22.6[a]
Gas	21.2	23.1	23.9
Combustible renewables (biomass) and waste[a]	10.9	–	–
Nuclear	6.9	6.2	4.2
Hydro	2.2	2.3	2.3
Other[b]	0.5	10.9	10.0
Total (%)[c]	100.0	100.1	100.0
Total (Mtoe)	10,029	12,100	14,800

[a] Includes combustible renewables and waste for OECD countries only.
[b] The 2001 data separate out combustible renewables (mostly wood and dung) and waste from "coal"; the IEA predictions for 2010 and 2020 report this item for OECD countries under "coal", and for non-OECD countries under "other"; this somewhat curious procedure explains the apparent increases attributed to renewables, which is most illusionary.
[c] IEA data have a rounding error of 0.1%.

At the start of the Industrial Revolution, the world population was only a few hundred million. Today, it stands at almost 6.9 billion people who collectively occupy around a billion dwellings, drive 800 million motor vehicles, and expend much effort to produce a wide variety of industrial products to further their well-being. Of the two billion people living without electric power, about one billion have no supplies of commercial energy in *any* form – not even petroleum or diesel oil. These people operate entirely on wood fuels and other biomass resources. Moreover, the disparity will intensify. It is generally expected that the world population will grow to an estimated 7.7 billion in 2020, and 90% of the growth will take place in the developing nations. Thus, over the next few decades, it is clear that global energy supply issues will move from the industrialised to the developing countries, many of which have serious social, economic, and environmental problems. Those that have coal will wish to burn it, despite the environmental consequences.

Of equal concern are the destructive effects of the growing levels of energy conversion and usage on the earth's biosphere. In global terms, the energy sector is the single largest source of anthropogenic greenhouse gases, with emissions of CO_2, methane, and nitrous oxide. At the local level, energy use in motor vehicles is a major contributor to the degradation of urban air quality. The exhaust pollutants include carbon monoxide, nitrogen oxides (NO_x), and hydrocarbons. Energy use in large stationary applications such as power stations is also a serious source of both sulphur oxides (SO_x) and NO_x, which are the major precursors to "acid rain". Fossil fuels are remarkable in the way that they are not just fuels, but also energy stores. Finding an economic means for storing energy, particularly electricity, lies at the heart of the renewables problem.

One prime form of keeping energy is to store it as hydrogen, which may be used to produce electricity in a fuel cell. Aspects of hydrogen storage and an overview of the chemical hydride technologies available for storing hydrogen are considered in the next section.

2. Hydrogen storage

Hydrogen can be stored as a compressed gas, as a liquid, in a chemical compound (*e.g.*, chemical hydrides or metal hydrides), or physically held within nanoporous structures. A major element of the cost of most of these storage modes (and a major consideration in terms of their energy efficiency) is the energy required to get the hydrogen in and out of the storage medium. Table 2 shows the cost of a number of storage means, including liquefaction, gas compression above the ground and underground, and chemical and metal hydrides.

In each case, the cost of the storage method is dependent on the cost of the requisite energy to get the hydrogen into the required form for storage, as well as on the scale and throughput, and sometimes on the storage medium. The storage can add anything from 0.1 € to 3.5 € kg^{-1} to the price of hydrogen (Table 2), depending on the storage means and assumptions on these associated variables.

Compressed gas and liquid hydrogen storage technologies are the current state-of-the art, but more compact means of storing hydrogen are needed for portable and mobile applications. Solid-state hydrogen storage materials would appear to be a very promising solution. However, they have in general low gravimetric capacity and, therefore, there has been a growing interest in the use of complex hydrides of the type of $Na^+[AH_x]^-$, where A represents boron or aluminium.

Sodium and lithium borohydrides are well-known reducing agents that are used in organic chemistry. For hydrogen storage, the aluminium salts $NaAlH_4$ and Na_3AlH_6 (the so-called "alanates") are the preferred reagents. Thermal decomposition of $NaAlH_4$ takes place in two steps, *i.e.*,

$$3NaAlH_4 \rightarrow Na_3AlH_6 + 2Al + 3H_2 \quad (1)$$

$$Na_3AlH_6 \rightarrow 3NaH + Al + 3/2H_2 \quad (2)$$

These reactions are reversible at elevated temperatures and pressures. The first step (Eq. (1)) at 323–373 K, corresponds to the release of 3.7 wt.% hydrogen and the second step (Eq. (2)), at 403–453 K, to a further 1.9 wt.% hydrogen. Research has shown that, in the presence of a titanium catalyst, the temperature for discharge and recharge of hydrogen may be brought down to acceptable levels. Titanium-catalysed $Na[AlH_4]$ has thermodynamic properties that are comparable with those of classic low temperature hydrides (*e.g.*, $LaNi_5H_6$ and TiFeH). Moreover, even if only the first step (Eq. (1)) can be utilised, the gravimetric hydrogen storage of $NaAlH_4$ is still more than that offered by AB, AB_2 or AB_5 hydrides. By contrast, Na_3AlH_6 requires higher temperatures for hydrogen liberation and might be useful to non-fuel applications such as pumping and heat storage. There are also complex hydrides based on transition metals, *e.g.*, Mg_2FeH_6. In most cases, they have low reversibility. The possibility of overcoming this limitation through development of efficient catalysts awaits further research.

Sodium borohydride, $NaBH_4$, is stable until about 673 K and is, therefore, not suitable for providing hydrogen through a thermal activation process. It does release hydrogen, however, on reaction with water, as described by Eq. (3).

$$NaBH_4 + 2H_2O \rightarrow NaBO_2 + 4H_2 \quad (3)$$

The borohydride hydrolysis reaction is irreversible, but has the advantage that 50% of the hydrogen comes from the water – in effect, $NaBH_4$ is a "water-splitting" agent. Based on the mass of $NaBH_4$, the hydrogen released corresponds to 21 wt.% – a remarkably high figure. Several of these so-called "chemical hydrides", *e.g.*, CaH_2, $LiAlH_4$, LiH, $LiBH_4$, KH, MgH_2, NaH, are being evaluated for their reactivity with water. One approach to preparing the storage medium is to mix the hydride with light mineral oil and a dispersant to form an "organic slurry". The oil coats the hydride

Table 2
Costs for various hydrogen storage technologies [6].

Technology	Transition scenario[a]	Cost range[b], € kg^{-1} H_2	Comments
Liquefaction (>45 kg h^{-1})	CHT, UH	0.8–1.2	Cost highly dependent on scale, efficiency, cost of electricity
Compressed gas (<1 week)[c]	CHT, UH, ES	0.1–0.5[d]	For stand-alone (*i.e.*, not on-board) storage only; strong economies of scale
Bulk underground	CHT, UH	0.1–0.2	Costs rise with increased storage time/reduced throughput
Chemical hydrides	CHT, UH, ES	1.2–1.9[e]	Large economies of scale, figures apply to 3.6 kto–9 Mto H_2; on-board storage
Metal hydrides	CHT, UH, ES	0.3–3.5	For storage times of 1–14 days; on-board storage
Methanol[f]	SLF	n/a	Cost not calculated; methanol can be produced from sources other than H_2

[a] Four scenarios: synthetic liquid fuels (SLF); central hydrogen for transport (CHT); ubiquitous hydrogen (UH); electricity stores (ES).
[b] Assuming that 1 € = 1.3 US$.
[c] Storage times of less than 1 week; cost rises with storage because H_2 throughput is reduced.
[d] One estimate is as high as 1.2 € kg^{-1} H_2; storage pressure not given in source.
[e] INCLUDES some energy and costs which could be regarded as H_2 production.
[f] NOT included in source table, but elsewhere in source.

particles and protects them from inadvertent contact with water, and also moderates the reaction rate of the hydride with water when desired.

The downside of using chemical hydrides is that the spent solution has to be returned to a processing plant for regeneration of the hydride. From the standpoint of mass, volume and cost, however, the system appears superficially to be attractive as a hydrogen-storage scheme for fuel-cell vehicles (FCVs). For example, Daimler AG has demonstrated that a $NaBH_4$ system, developed by Millenium Cell in the USA, can provide a minivan (the "Natrium") with a range of 480 km. Much will depend on the difficulty and cost of the reprocessing operation. At the service station, instead of refuelling with hydrogen gas, the vehicle would have its tank emptied and refilled with fresh hydride slurry. This is similar to the procedure proposed for the zinc-air traction battery.

Organic liquids, such as cyclohexane or methanol, and nanostructured materials are other possible approaches to chemical storage of hydrogen, but borohydrides, namely sodium borohydride, with their enormous potentialities as hydrogen storage materials and as fuels, are considered a topic requiring further attention. This is the main subject of the present paper, to be detailed in the following sections.

3. Synthesis of sodium borohydride

Borohydrides belong to a class of materials with the highest gravimetric hydrogen densities. There are many types of borohydrides depending on the composition of M, B and H, *e.g.*, $M(BH_4)_n$, $M(B_3H_8)_n$, $M(B_6H_6)_n$, $M(B_9H_9)_n$ and $M(B_{12}H_{12})_n$ [7].

Here, we focus on sodium borohydride, $NaBH_4$, which has a hydrogen-rich anion, the borohydride, BH_4^-, which is similar to AlH_4^- (alanate) in $NaAlH_4$. Moreover, $NaBH_4$ has a higher gravimetric hydrogen density than $NaAlH_4$, due to B being lighter than Al. On the other hand, $NaBH_4$ does not release hydrogen by the same reaction pathways of alanate, *e.g.*, $NaAlH_4$ to Na_3AlH_6. Therefore, confirmation of similarity and difference between $NaBH_4$ and $NaAlH_4$ is important.

$NaBH_4$ is not a new compound since it was discovered in the 1940s [8]. In fact, the first report of a pure alkali metal borohydride appeared in 1940 by Schlesinger and Brown who synthesised $LiBH_4$ by the reaction of ethyllithium with B_2H_6 [9]. The direct reaction of the corresponding metal/metal hydride with diborane in ethereal solvents under suitable conditions produces high yields of the borohydride compound [10–12]:

$$2MH + B_2H_6 \rightarrow 2MBH_4 \quad (M = Li, Na, K) \tag{4}$$

Schlesinger and Brown also discovered $NaBH_4$ in 1940, while leading a team that developed metal borohydrides for wartime applications, but their work involving $NaBH_4$ was classified and published in a scientific journal only in 1953 [10,13,14], although a patent had been granted 3 years before [15].

Thus far, about 100 methods for preparation of $NaBH_4$ have been suggested in the last 60 years. Fig. 1a shows that the number of published papers concerning the synthesis of $NaBH_4$ has seen a considerable increase in the last decade [10,13,14,16–51], mainly due to the recent wave of interest on $NaBH_4$ for energy systems. Besides the papers in scientific journals, and given the importance of achieving a cheap method for $NaBH_4$ production, it seems natural that many patents have also been published on this matter. Fig. 1b shows that over 78 patents have been granted to processes that claim the $NaBH_4$ synthesis [12,15,52–127]. It is interesting to notice the occurrence of two separate time periods with high number of patents on the $NaBH_4$ synthesis: the first one was in the sixties, following the $NaBH_4$ discovery; the second peak was already in the 21st century, caused by the recent demand for alternative energy power sources (Fig. 1b).

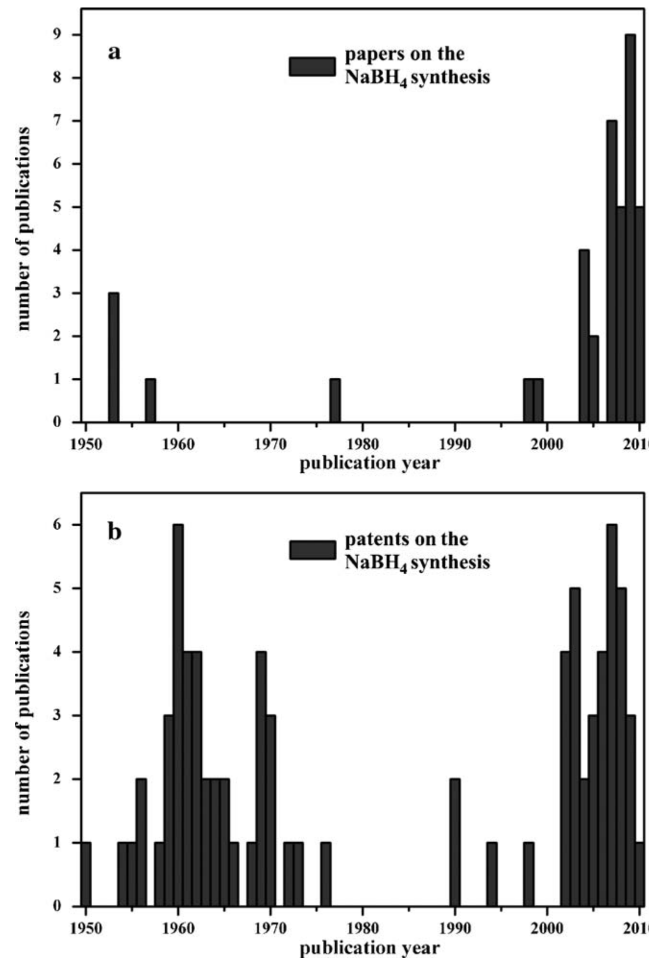


Fig. 1. Evolution of the number of publications regarding the synthesis of $NaBH_4$: (a) journal papers and (b) patents.

Industrial production of $NaBH_4$ using the Brown–Schlesinger process is carried out by the reaction of extremely fine sodium hydride with trimethyl borate in high boiling hydrocarbon oil at about 523–553 K [14,15]:

$$4NaH + B(OCH_3)_3 \rightarrow NaBH_4 + 3NaOCH_3 \tag{5}$$

The other industrial $NaBH_4$ synthesis process was developed by Bayer and uses finely grounded borosilicate glass, sodium and hydrogen [17]:

$$Na_2B_4O_7 + 7SiO_2 + 16Na + 8H_2 \rightarrow 4NaBH_4 + 7Na_2SiO_3 \tag{6}$$

The $NaBH_4$ material is then extracted from the borohydride–silicate mixture with liquid ammonia under pressure.

Different approaches to the synthesis of $NaBH_4$ have recently been reviewed by Santos and Sequeira [51]. They consider synthetic processes that are or have been in operation on an industrial scale; potential routes based on direct use of carbon, hydrocarbons, or hydrogen reducing agents; multi-step thermochemical reaction pathways that were developed to address the inadequacies of the former direct reactions, and which take advantage of the characteristic disproportionation chemistry of boron compounds; reaction pathways that use metals as reducing agents; and alternative energy sources such as microwaves and nuclear radiation.

In essence, the Brown–Schlesinger and Bayer processes are both electrochemical in nature, given that the majority of the energy needed to make $NaBH_4$ is introduced into the system in the form of electricity used to make sodium metal.

As done for the thermal reaction processes, it makes sense to discuss the most desirable electrochemical reactions for the $NaBH_4$ synthesis, and then examine their flexibility. Cooper [87], Hale and Sharifian [89], Sharifian and Dutcher [90], Sun and Liang [100], and Guilbault et al. [106] are among those who have reported the electrochemical conversion of borate to borohydride in aqueous media, but studies by Gyenge and Oloman [18] and by Calabretta and Davis [28] failed to verify that any borohydride was synthesised in the electrochemical systems used by Cooper, Hale and Sharifian [87,89,90]. $NaBH_4$ electrosynthesis attempts in aqueous media, molten salts, and ionic liquids have also been carried out in our laboratory [51], as briefly summarised hereinafter.

The electrosynthesis of $NaBH_4$ in aqueous media has been attempted in a two-compartment electrolytic cell using alkaline catholyte solutions containing sodium metaborate ($NaBO_2$), or sodium tetraborate ($Na_2B_4O_7$), with and without hydrogen poisons (*e.g.*, thiourea), sodium hydroxide aqueous anolyte solutions, and Nafion 117 and other permselective membranes to separate the two compartments. Platinum, palladium, cadmium, nickel, gold, zinc, lead, mercury, graphite, stainless steel and other materials, were tested as cathodes. As for the anode material, nickel, platinum, graphite and stainless steel, were used. The polarisation behaviour of the electrodes was controlled to guarantee that cathode potentials more negative than the discharge potential required for the borohydride production (≤ -1.46 V vs. SHE) were attained during the electrolytic operation [51].

The aqueous electrosynthesis of $NaBH_4$, starting from $NaBO_2$, is described by the overall reaction shown in Eq. (7),

$$NaBO_2 + 2H_2O \rightarrow NaBH_4 + 2O_2 \quad (7)$$

with the cathodic and anodic partial reactions being given by Eqs. (8) and (9), respectively.

$$NaBO_2 + 6H_2O + 8e^- \rightarrow NaBH_4 + 8OH^- \quad (E^0 = -1.24\,V\,vs.\,SHE) \quad (8)$$

$$8OH^- \rightarrow 2O_2 + 4H_2O + 8e^- \quad (E^0 = 0.40\,V\,vs.\,SHE) \quad (9)$$

Assuming that the applied cathodic overpotential is sufficient to achieve complete conversion of the $NaBO_2$ into $NaBH_4$ within the test solution, and there are no side reactions (*e.g.*, hydrogen evolution and/or borohydride hydrolysis), the integrated charge is expected to rise asymptotically with time towards a value of znF (z is the number of moles of transferred electrons – 8 – per mole of $NaBO_2$, n is the number of moles of $NaBO_2$ present and F is Faraday's constant).

Regarding the $NaBH_4$ electrosynthesis attempts in molten salts, the analysis of the most suitable electrolytes for the reaction medium revealed that NaOH should be part of the molten electrolyte. NaOH provides the OH^- ions for the oxidation at the anode, the Na^+ ions for the ionic conduction through the separator, stabilises the produced $NaBH_4$ in the catholyte, and enables the preparation of low melting point eutectic compositions for the $NaBO_2$ electrolysis. A eutectic mixture composed of NaOH (51%) + KOH (49%) (in molar%), having a melting point of 443 K, was used as the molten electrolyte medium for the $NaBH_4$ synthesis. This system showed problems concerning the electrodes' stability, need for controlled atmosphere, nature of the metal electrocatalyst, the type of the separator material, and water contamination, among others.

Table 3
Physical and chemical properties of sodium borohydride.

Appearance	White to grey-white microcrystalline powder or lumps
Odour	Odourless
Solubility	Soluble in water; reacts with hot water
Specific gravity	1.074
% Volatiles by volume at 294 K	0
Melting point	778 K (10 atm H_2)
Vapour density (air = 1)	1.3

The $NaBH_4$ electrosynthesis reaction has also been studied in ionic liquids medium. Two ionic liquids (octamethylimidazolium and 1-butyl-1-methylpyrrolidinium trifluoromethanosulphonate) were selected and characterised as possible electrolyte medium for the synthesis. However, both ionic liquids displayed low ionic conductivity. Moreover, the tested ionic liquids displayed good solubility for NaOH and $NaBH_4$ but high insolubility for $NaBO_2$. Experience gained with available ionic liquids does not make them particularly attractive for bulk electrolysis. Nevertheless, our group at TU Lisbon is developing ways to minimise present limitations, namely by: (i) increasing the working temperature to decrease the ionic liquid viscosity; (ii) using ultrasonication to assist mass transport; (iii) bubbling nitrogen gas through the solution to enhance mass transport; (iv) minimising the volume of bulk electrolysis cell; (v) using a high area working electrode to optimise the area to ionic liquid volume ratio; (vi) using a flow cell or other hydrodynamic methods (*e.g.*, stirring) to enhance mass transport; and (vii) employing a mixture of an ionic liquid and a low viscosity highly volatile organic solvent (*e.g.*, dichloromethane) to lower the viscosity. The volatile organic solvent may then be removed under vacuum conditions after completion of the bulk electrolysis experiment. It is believed that the recent advances in the chemistry of ionic liquids will soon render an effective electrolytic medium for $NaBO_2$ conversion to $NaBH_4$ [128].

Based on the obtained results, it is anticipated that much work is still required to fully understand how the electrochemical approach can be used in the synthesis of $NaBH_4$.

4. Properties of sodium borohydride

4.1. General

Sodium borohydride, also known as sodium tetrahydridoborate (or tetrahydroborate), has the chemical formula $NaBH_4$ (CAS 16940-66-2). It is a white solid, usually available as a powder or confectioned in pellets, that melt at 778 K and 10 atm H_2. $NaBH_4$ is hygroscopic, decomposing slowly at temperatures above 673 K [129].

$NaBH_4$ is a selective speciality reducing agent used in the manufacture of pharmaceuticals, intermediates and fine chemicals. $NaBH_4$ converts aldehydes and ketones into alcohols but, unlike $LiAlH_4$ (also widely used as a reductant), $NaBH_4$ does not react with esters, amides, or carboxylic acids.

Table 3 presents some general physical and chemical properties of $NaBH_4$, and Table 4 shows its stability conditions.

Fig. 2 gives an idea of the number of published journal papers devoted to the characterisation of $NaBH_4$ [130–178]. The number of papers per decade has been relatively constant until the 21st century, with a natural increase in recent years.

Industrially, $NaBH_4$ is an important starting material for the production of other borohydrides. For example, KBH_4 is produced on an industrial scale by the following metathesis reaction:

$$NaBH_4 + KOH \rightarrow KBH_4 + NaOH \quad (10)$$

Alkaline-earth borohydrides, trivalent and tetravalent borohydrides, $M(BH_4)_n$ (M = alkaline-earth, groups 3–14 in the periodic

Table 4
Stability of sodium borohydride.

Stability	Hygroscopic; stable in dry air up to 573 K; decomposes slowly in moist air or vacuum above 673 K
Hazardous decomposition products	Sodium oxide and hydrogen gas
Incompatibilities	Reacts with water to evolve hydrogen; excessive heat decomposes it to sodium metaborate, releasing hydrogen gas; may react slowly or vigorously with acids or certain transition metal catalysts to liberate hydrogen; incompatible with oxidising agents, sulphuric acid, ruthenium salt and metal salts
Conditions to avoid	Moisture, heat, flame, ignition sources, air and incompatibles

table, n = valence of M) are synthesised by the metathetical reaction, as follows:

$$n\text{NaBH}_4 + \text{MX}_n \rightarrow \text{M(BH}_4)_n + n\text{NaX} \quad (11)$$

Here, X = halogen, such as F, Cl, Br, I. These metathetical reactions occur with certain elements of M, *e.g.*, group 2 (magnesium, etc.) [179–181], groups 4, 13, etc. For example, Konoplev and Bakulina [179] have synthesised $Mg(BH_4)_2$ by reaction of $NaBH_4$ and $MgCl_2$ in molar ratio 2.7–3.8:1 in diethyl ether (2:1 stoichiometry). After progression of the metathetical reaction (Eq. (11)), the precipitated NaCl is filtered, and then the $Mg(BH_4)_2$ ether solution is evacuated at 453 K in order to remove diethyl ether.

Multi-cation borohydrides, $MM'(BH_4)_n$ (M = alkaline metals, M′ = other metals) have been synthesised by the reaction described in Eq. (12) [182].

$$m\text{MBH}_4 + \text{M}'\text{Cl}_n \rightarrow \text{M}_{m-n}\text{M}'(\text{BH}_4)_m + n\text{MCl} \quad (12)$$

There are many kinds of multi-cation borohydrides with coordinated solvents. For example, multi-cation compounds, such as $Li_3(BH_4)(NH_2)_2$ have been reported [183]. Those borohydrides might be useful for controlling the thermodynamic stability, similar to the conventional "alloying" method for hydrogen storage materials [182].

The solubility of $NaBH_4$ in various solvents is summarised in Table 5. In protic solvents, solvolysis occurs for $NaBH_4$, and hydrogen is released as follows:

$$\text{NaBH}_4 + 4\text{ROH} \rightarrow \text{NaB(OR)}_4 + 4\text{H}_2 \quad (13)$$

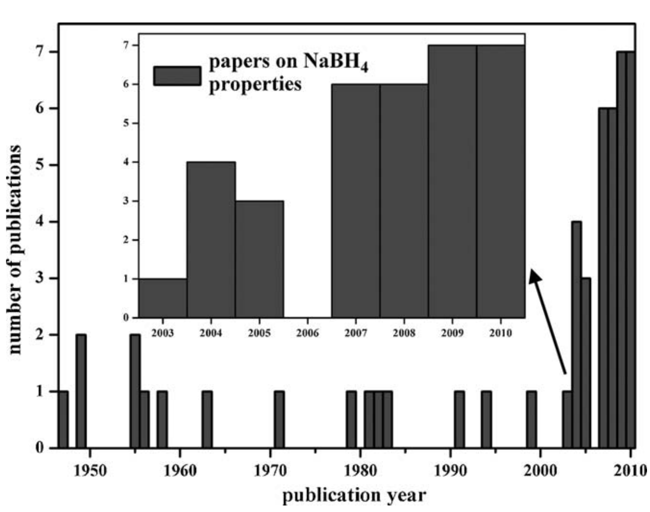


Fig. 2. Evolution of the number of publications regarding sodium borohydride properties.

Table 5
Solubility of sodium borohydride in various solvents (g/100 g solvent at 298 K).

	T_b of solvent (K)	$NaBH_4$ solubility
Water	373.0	55
Methanol	310.7	16.4[a]
Ethanol	351.5	4.0[a]
Isopropylamine	307.0	6.0[b]
Diethyl ether	309.0	Insol.
THF	338.0	0.1[c]
Diglyme	435	5.5
Toluene	384	Insol.
Ammonia	239.7	104
DMF	426	18.0[d]

Adapted from [129].
[a] 293 K, decomposition.
[b] 301 K, decomposition.
[c] 293 K, decomposition.
[d] Dangerous decomposition possible at higher temperature.

Here, ROH is, for example, methanol or ethanol. Because $NaBH_4$ decomposes up to 80% after 1 h in methanol at 273 K (and 6% after 1 h in ethanol), excess $NaBH_4$ is used for this synthesis reaction (Eq. (13)).

4.2. Crystal structure

There have been many recent works devoted to the study of the crystal structure of $NaBH_4$ (and other borohydrides) [161,172,176]. Some data on the crystal structure of $NaBH_4$ [151] is summarised in Table 6.

$NaBH_4$ shows NaCl-type structure at ambient conditions [130,151,184]. The lattice constants and distances between Na and B depend, of course, on the Na atomic number. However, the distances between B and H, *i.e.*, the size of the BH_4^- tetrahedra, are almost the same, independent of the alkali metal (Na, Li, K, Rb, Cs). $NaBH_4$ shows structure transition at low temperature; it crystallises in tetragonal $P4_2/nmc$ below 190 K [152]. At 6.3 GPa, $NaBH_4$ has a structure transition to tetragonal $P42_1C$, with lattice constants a = 4.0864(1) Å, c = 5.5966(7) Å, and to orthorhombic *Pnma*, with a = 7.33890(1) Å, c = 5.6334(5) Å, at a pressure of 6.3 and 8.9 GPa, respectively [185].

4.3. Electronic structure

The electronic structure of $NaBH_4$ has been investigated by first-principles calculations. The electronic structure is non-metallic with the calculated energy gap of 6.8–7.0 eV [152]. Because there is little contribution of Na orbitals to the occupied states, Na atoms are thought to be ionised as Na^+ cations. The occupied states split into two peaks: the low energy states are composed of B-2s and H-1s orbitals and the high-energy states consist of B-2p and H-1s orbitals. A boron atom constructs sp^3 hybrids and forms covalent bonds with surrounding four H atoms. The charge from the extra electron needed to form these bonds is compensated by a Na^+ cation. This character is also confirmed experimentally by synchrotron X-ray diffraction measurement and maximum entropy method (MEM) analysis [152]. The calculated total density of state (DOS) for $NaBH_4$ is displayed in Fig. 3 [152]. The compound has

Table 6
Crystal structure of sodium borohydride at room temperature [151].

Structure	Cubic
Space	*Fm*−3*m*
Group	No. 225
Lattice constants (Å)	a = 6.1506 (6)
Na–B distance (Å)	3.0753 (3)
B–H distance (Å)	1.17078 (6) × 4

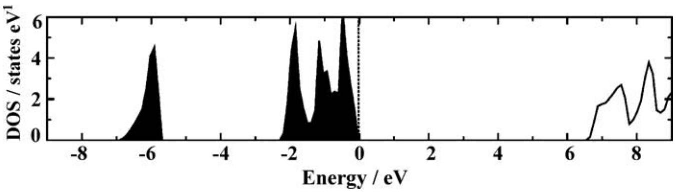


Fig. 3. Calculated ground-state total DOS for $NaBH_4$. Fermi level is set at zero energy and marked by the vertical dotted line; occupied states are shaded.
Adapted from [152].

finite energy gap between the valence and conduction bands. Hence it is a proper insulator with an estimated band gap of ~5.5 eV.

5. Methods for sodium borohydride monitoring

Most existing methods for borohydride determination are neither easy nor fast [186]. These include hydrogen evolution [132,187], acid–base titration [132], iodate [188], hypochlorite [189], and voltammetric procedures [191]. Fig. 4 shows that the number of published papers devoted to methods for the $NaBH_4$ monitoring is not very large [132,188–210].

The development of simpler and faster methods for $NaBH_4$ determination, either from a quantitative or from a qualitative point of view, would be very helpful for the scientific community working in any applications involving $NaBH_4$, *e.g.*, energy systems (direct borohydride fuel cells, $NaBH_4$ for hydrogen production and storage), in $NaBH_4$ synthesis, for electrodeposition purposes, as reducing agent in organic synthesis, etc. Our group has studied several typical analytical methods for $NaBH_4$ monitoring, as well as a quick and simple potentiometric technique for the *in situ* monitoring of small $NaBH_4$ concentrations. Most of these methods were initially tested in our laboratory for application in $NaBH_4$ electrosynthesis studies (Section 3).

The well known iodate method [189] is based on the reaction of $NaBH_4$ with KIO_3. Addition of KI and acid convert the excess iodate into iodine, which is then titrated with thiosulphate. This volumetric method was proven to be extremely time-consuming and leading to erroneous results, being promptly abandoned.

A new "hydride hydrolysis" test (Fig. 5) was developed based on the gasometric measurements of the hydrogen generated

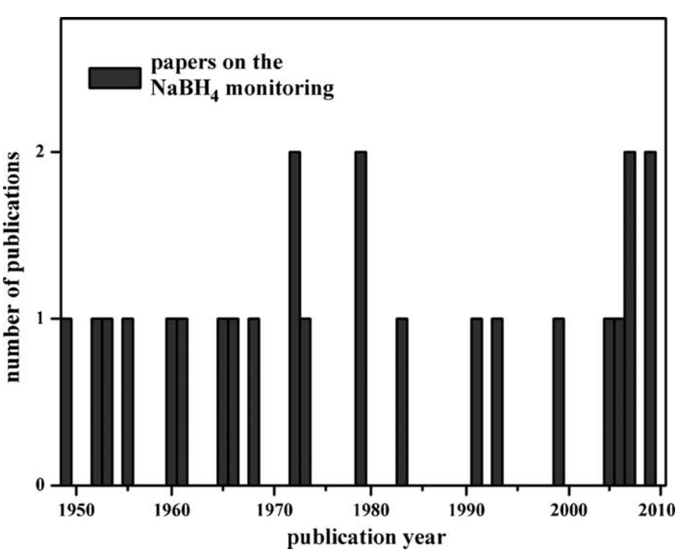


Fig. 4. Evolution of the number of publications regarding the borohydride monitoring.

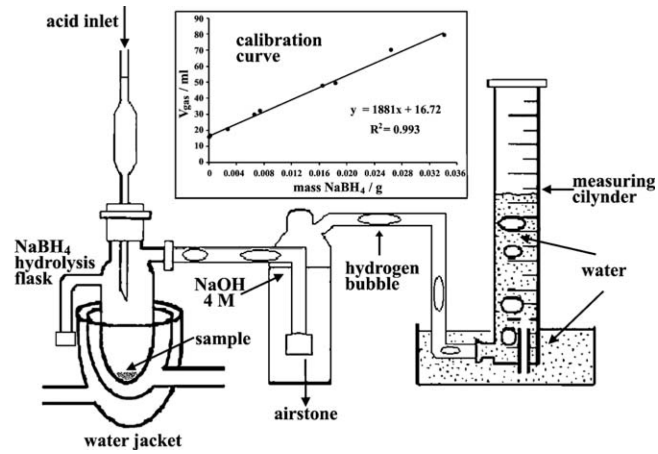


Fig. 5. Experimental setup used for the gasometric measurements of the hydrogen generated on product sample hydrolysis and example of calibration curve used for $NaBH_4$ determination.

by the decomposable borohydride product resulting from the electrosynthesis experiments (Section 3), being assisted by a calibration curve for pure $NaBH_4$. This new method shows good reproducibility but requires further design optimisation to reduce its detection limit [51].

The use of infrared (IR) spectroscopy analysis (Fig. 6) has shown that the three B–H bond stretching vibration bands observed in the $NaBH_4$ electrosynthesis reaction products [51] are in good agreement to the ones obtained for pure $NaBH_4$ and with the values found in the literature [146,160,191].

Table 7 presents data taken from the IR spectra of the electrosynthesis product and of a sample of $NaBH_4$ p.a. The values obtained experimentally are compared to previous data available in the open literature. Although this method is able to detect the presence of borohydride in the electrosynthesis products, IR spectroscopy analysis has the disadvantage of taking excessive time. In fact, it requires full drying of the reaction products and preparation of a KBr/sample pellet suitable for the IR spectrophotometer [51].

The experience gained on the monitoring of the $NaBH_4$ electrosynthesis indicated that electrochemical methods should be appropriate to follow the reaction process.

In 1999, Amendola et al. [204] reported the non-destructive *in situ* detection of relatively low $NaBH_4$ concentrations by an undemanding method that is in essence a potentiometric titration technique. The method was simply based on the change of the open circuit potential (OCP) of a given metal with the $NaBH_4$ concentration.

In the majority of potentiometric measurements, the potential of one electrode is kept constant, with this electrode being referred to as the reference electrode. The second electrode responds to the activity or concentration of the species contained in the solution under investigation and is referred to as the indicator electrode. Amendola et al. [204] used platinum, rhodium, and cobalt as metal indicator electrodes.

Table 7
B–H bond stretching vibrations for sodium borohydride.

	ν (B–H)/cm^{-1}
Electrosynthesis product	2225, 2293, 2359
$NaBH_4$ p.a.	2224, 2290, 2387
$NaBH_4$ [191]	2229, 2305, 2400
$NaBH_4$ [146]	2217, 2284, 2404
$NaBH_4$ [160]	2216, 2282, 2396
$NaBH_4 \cdot 2H_2O$ [160]	2221, 2268, 2380

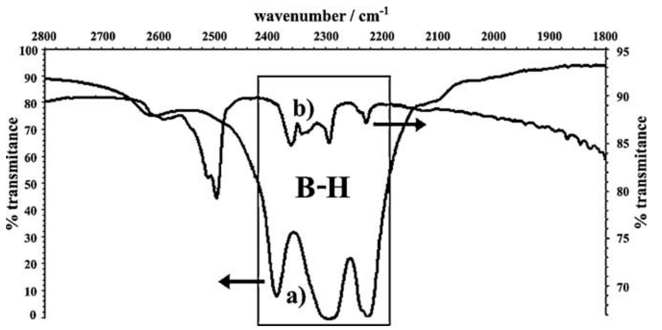


Fig. 6. Infrared spectra taken for $NaBH_4$ p.a. (a), and for the electrosynthesis reaction product obtained in aqueous medium (b).

In order to develop the method originally proposed by Amendola et al. [204], several materials (*e.g.*, Pt, Pd, Cd, Au, Cu, Ni, Fe, AISI 304 stainless steel, Zn, Mo, Nb, graphite, and Si) were tested as indicator electrodes for $NaBH_4$ monitoring [209]. It was shown that the materials whose OCP is significantly different when immersed in NaOH supporting electrolyte with or without $NaBH_4$ may be candidate indicator electrodes for application in a novel borohydride microelectrode sensor. The potentiometric procedure for a gold (Au) indicator electrode led to the curve shown in Fig. 7.

Fig. 7 shows that the Au OCP starts to decrease for $NaBH_4$ concentrations above 10^{-2} M, with an OCP response range of about 1 V. Similar curves were recorded for other tested indicator electrode materials [209] and available thermodynamic data [211–213] helped in the analysis of the obtained OCP–[$NaBH_4$] plots. According to the $NaBH_4$ concentration ranges where the OCP changes take place, the six selected materials presented in Fig. 8 can be classified as the top indicator electrode materials for each specific $NaBH_4$ concentration range.

6. Sodium borohydride hydrolysis and dehydriding

In 1954, Schlesinger et al. [10] reported that $NaBH_4$ reacts slowly with water to liberate four moles of hydrogen per mole of $NaBH_4$, equivalent to 2.5 l of hydrogen per gram of $NaBH_4$, at

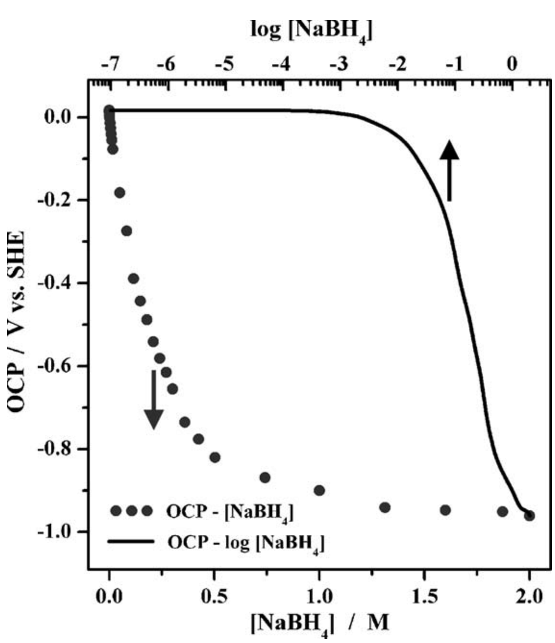


Fig. 7. OCP change as a function of the $NaBH_4$ concentration for an Au electrode in 4 M NaOH solution at 298 K [209].

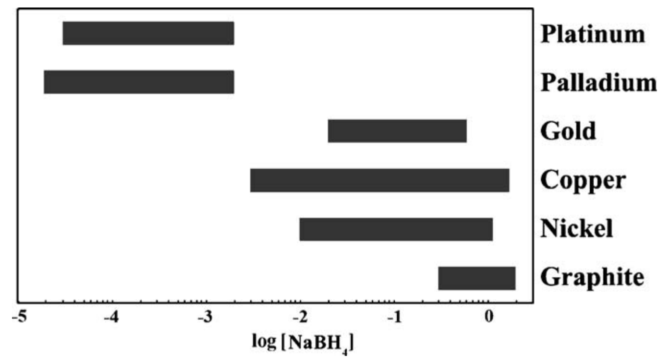


Fig. 8. Top materials displaying steeper OCP changes for specific borohydride concentrations [209].

room temperature. The reaction (Eq. (3)) could be accelerated by rising the temperature or by adding acids/catalysts. By then, the Schlesinger group had tested the catalytic effects of more than 20 acids and of certain metal salts (manganese (II), iron (II), cobalt (II), nickel (II), and copper (II) chlorides) [214]. Historically, their observations have been crucial because they have introduced two features that are central today: $NaBH_4$ generates hydrogen; and this hydrogen generation can be catalytically accelerated.

Nowadays, many papers entirely devoted to the $NaBH_4$ hydrolysis have been published [38,214–426]. Fig. 9 shows that the focus on the borohydride hydrolysis suffered an almost exponential increase in the beginning of the 21st century, showing a maximum of 47 publications during the year of 2008.

Levy et al. [215] reported that the $CoCl_2$-catalysed hydrolysis is a first-order reaction with respect to the $NaBH_4$ concentration and that an application of kinetic data should allow a precise selection of the catalyst concentration required to give the desired hydrogen generation rates. Brown and Brown [216] showed that many of the heavy metals exerted a powerful catalytic effect on the hydrolysis of $NaBH_4$. The platinum family metals were unusually effective, following the order Ru, Rh > Pt > Co > Ni > Os > Ir > Fe ≫ Pd, at 298 K. $NaBH_4$ reduced the platinum metals to the elementary state, in a form which exhibited high catalytic activity for the hydrolysis reaction. Davis et al. [217] focused on the hydrolysis catalysed by general acids (Eq. (14)).

$$BH_4^- + H_3O^+ + 2H_2O \rightarrow H_3BO_3 + 4H_2 \quad (14)$$

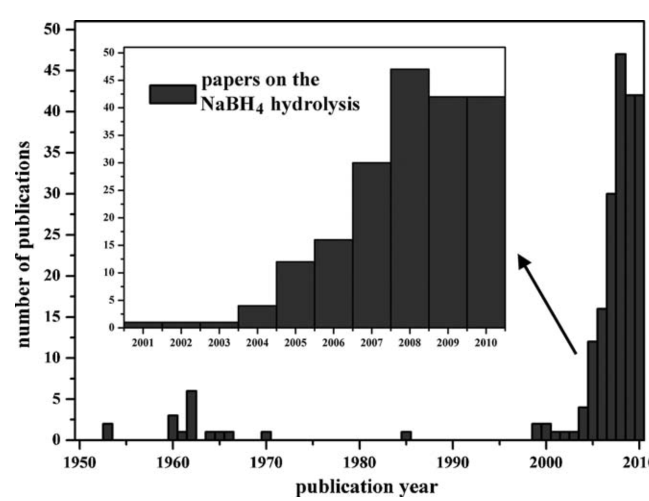


Fig. 9. Evolution of the number of publications regarding the borohydride hydrolysis.

The reaction order was unitary in relation to the $NaBH_4$ concentration and unitary to the concentration of the acid. Many studies attempting to understand the $NaBH_4$ hydrolysis reaction kinetics and mechanisms were then published [217–220].

The hydrogen generation in other solvents, like alcohols [403,427,428], was also assessed. Davis and Gottbrath [428] investigated the reaction of $NaBH_4$ with methanol (methanolysis). Hydrogen gas is produced according to Eq. (15), which is, as expected, of the same type as Eq. (13).

$$NaBH_4 + 4CH_3OH \rightarrow NaB(OCH_3)_4 + 4H_2 \quad (15)$$

The reaction order vs. the $NaBH_4$ concentration was found to be of one. It was besides reported that the addition of an acid increased the rate of methanolysis while basic materials decreased it.

The generation of hydrogen by complete dehydriding of $NaBH_4$ is described by Eq. (16) [156].

$$NaBH_4 \rightarrow NaH + B + 3/2H_2 \quad (16)$$

The dehydriding reaction of $NaBH_4$ liberates 8 wt.% H_2 at above the boiling temperature (838 K) and decomposes into NaH and B. The enthalpy change of the dehydriding reactions, ΔH_d, is 66 kJ mol^{-1} H_2 [156,429,430]. The heat of formation of $NaBH_4$, ΔH_{boro}, may be estimated from the difference of the total energies between the left and right-hand sides of Eq. (17).

$$Na + B + 2H_2 \rightarrow NaBH_4 \quad (17)$$

The bonding character between Na^+ and BH_4^- in $NaBH_4$ is ionic, and the charge transfer from Na^+ to BH_4^- is responsible for the stability of $NaBH_4$. The ability of the charge transfer can be measured by the electronegativity. There is a good correlation between ΔH_{boro} and the Pauling electronegativity of the metal cation. This is 0.9 for Na, so the predicted heat of formation for $NaBH_4$ is given by Eq. (18).

$$\Delta H_{boro} = 253.6 \times 0.9 - 398.0 = -169.8\ \text{kJ mol}^{-1} \quad (18)$$

The estimation of ΔH_d for $NaBH_4$ not only takes into account the stability of $NaBH_4$ but also the stability of the products. Therefore, ΔH_d is estimated using predicted ΔH_{boro} and known values of $\Delta H_{product}$ [431] (Eq. (19)).

$$\Delta H_d = \Delta H_{boro} - \Delta H_{product} \quad (19)$$

So, as reported above, ΔH_d for $NaBH_4$ is 66 kJ mol^{-1} H_2 and the decomposition temperature, T_d, is 838 K, which is the boiling temperature. A thermodynamic unstable borohydride is expected only for metal cations for which the Pauling electronegativity is larger than 1.5.

In the hydriding and dehydriding reactions of $NaBH_4$, not only hydrogen but also other elements should be diffused. This is not the same as conventional metal hydride alloys in which diffusion of hydrogen and expansion of lattice for the alloy is dominant. Generally, the fast diffusion of elements is very difficult in the solid state at much lower than the melting temperature. Therefore, the observed T_d during heating process seems to become higher than that predicted. Moreover, a hydrogen pressure (generally more than 10 MPa) higher than that predicted for ΔH_d is required for hydriding of $NaBH_4$. This is why a high temperature is required for diffusion of elements, at which high hydrogen pressure should be applied for hydriding. Therefore, solving the kinetic problem is an important area of research in the use of complex hydrides as hydrogen storage materials.

In order to improve the reaction kinetics, ball milling and addition effects (doping) have been investigated. Barkhordarian et al. [27] reported that the kinetic barriers for the formation of $NaBH_4$ are drastically reduced when MgB_2 is used instead of B as the starting material for the hydriding reaction, with simultaneous reduction of the reaction enthalpy in ~10 kJ mol^{-1} H_2.

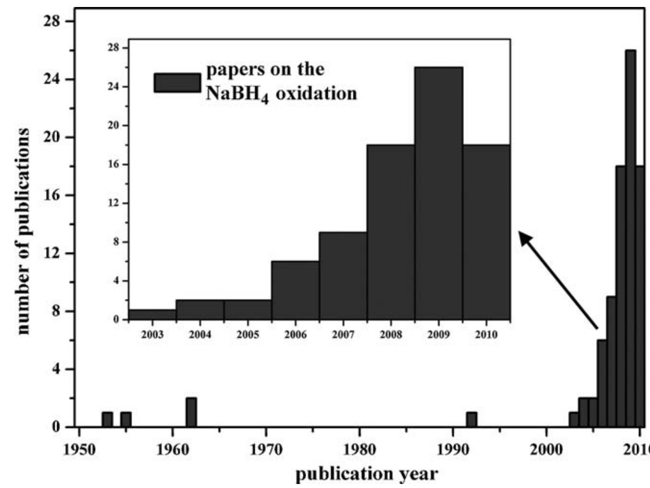


Fig. 10. Evolution of the number of publications regarding the borohydride oxidation.

7. Oxidation of sodium borohydride

The oxidation of $NaBH_4$ was studied for the first time in 1953, by Pecsok [426], who proposed the net reaction for the polarographic oxidation of the borohydride ion, BH_4^-, described by Eq. (20).

$$BH_4^- + 8OH^- \rightarrow BO_2^- + 6H_2O + 8e^- \quad (20)$$

The standard electromotive force, E^0, of this half reaction was calculated as being 1.21 V vs. the standard hydrogen electrode (SHE) and it was observed that the BH_4^- oxidation was irreversible. Two years later, Stockmayer et al. [133] calculated an E^0 value of 1.24 V vs. SHE. In 1962 [432,433] and 1992 [434] three more publications dealt with the BH_4^- oxidation, but it was only from 2003 onwards that a large number of papers were published on the subject (Fig. 10).

In fact, during the last 7 years more than 80 papers have been published on exploratory fundamental research on the $NaBH_4$ electrooxidation [133,165,426,432–514]. In our laboratory, we have undertaken systematic studies on the BH_4^- electrooxidation in several catalytic and noncatalytic electrode materials, using various concentrations of $NaBH_4$ and NaOH, and at different working temperatures [495–497]. Well-established electrochemical methods, namely chronopotentiometry, chronoamperometry, chronocoulometry, and cyclic voltammetry, were used to better understand the BH_4^- anodic process. As electrode material, Au was selected because of its high catalytic activity for the BH_4^- oxidation reaction (with a number of exchanged electrons, n, close to the theoretical value of 8) and because of its relatively low catalytic activity for the concurrent detrimental BH_4^- hydrolysis reaction.

Potential step experiments [495] were carried out at temperatures ranging from 298 to 338 K and imposed potentials from 0.05 to 0.45 V vs. SHE. The supporting electrolyte was 2 M NaOH and the $NaBH_4$ concentrations varied from 0.03 to 0.12 M. The Cottrell equation was applied to the obtained chronoamperometric curves, where diffusion prevailed, to determine the diffusion coefficient, D. Arrhenius plots of the D values led to diffusion activation energies, E_d, of 16.6, 15.6 and 20.5 kJ mol^{-1}, and maximum diffusion coefficients, D_0, of 1.55×10^{-2}, 9.56×10^{-3}, and 5.13×10^{-2} cm^2 s^{-1}, respectively, for the tested $NaBH_4$ concentrations of 0.03, 0.06 and 0.09 M. Chronocoulometric experiments [495] led to Anson plots (q vs. $t^{1/2}$), from which it was possible to calculate accurate apparent rate constants for electron transfer. Activation energies for charge

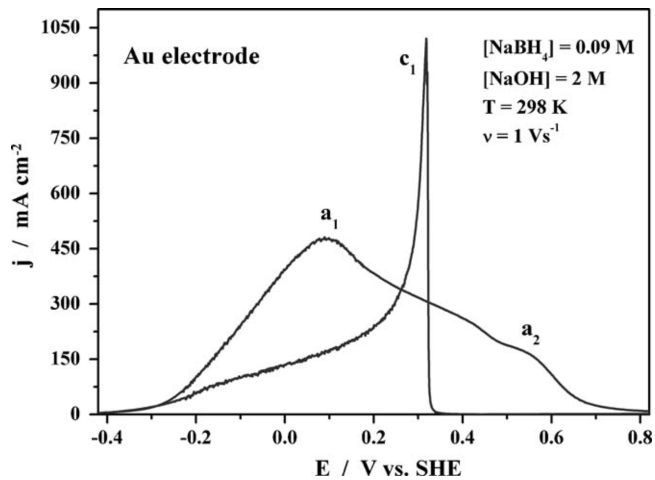


Fig. 11. Typical CV obtained at 1 V s^{-1} on a Au electrode in 2 M NaOH + 0.09 M $NaBH_4$ solution, at 298 K.

transfer could then be obtained. The analysis of the $i - t$ transients in the mixed control region allowed extending the Tafel plots to determine exchange current densities, j_0, anodic transfer coefficients, α, and consequently, the standard heterogeneous rate constants, k_s. From the $\ln k_s$ vs. T^{-1} plots, it was found that the standard activation energies for charge transfer, E^0_{ct}, in the Au/$NaBH_4$ system were 10.8, 25.2, 37.2 and 43.3 kJ mol^{-1}, for the $NaBH_4$ concentrations of 0.03, 0.06, 0.09 and 0.12 M, respectively [495].

Using the same experimental conditions, applied current densities in the range of 10–1000 mA cm^{-2} were carefully selected to guarantee that the chronopotentiometric data [496] are collected in a domain where the Sand equation is valid. A single oxidation wave was always observed for concentration ratios [NaOH]/[$NaBH_4$] > 4.4.

From our chronopotentiometric results and complementary chronoamperometric data [437], the overall BH_4^- oxidation process was shown to be irreversible involving a number of electrons close to the theoretically expected value of 8. Linear E vs. $\log(\tau^{1/2} - t^{1/2})$ plots, where τ is the transition time, were obtained, and this well-known diagnostic criterion enabled concluding that for the studied potential and $NaBH_4$ concentration ranges (*i.e.*, −0.25 to +1.75 V vs. SHE; 0.03 to 0.12 M), the rate-determining step is an irreversible, diffusion-controlled, one-electron oxidation step for which several key kinetic parameters (α, k_s, E^0_{ct}) were calculated [496].

Further studies of the BH_4^- electrooxidation on a Au disc macroelectrode in 2 M NaOH solutions were performed by cyclic voltammetry [497]. Voltammograms were obtained for $NaBH_4$ solutions of various concentrations, working temperatures, and potential scan rates ranging from 0.02 to 20 V s^{-1}, over a wide potential range (−0.7 to 1.0 V vs. SHE). A typical CV for the borohydride oxidation in a Au electrode is shown in Fig. 11.

Basically, there is a well-defined anodic peak (a_1) around 0.1 V (vs. SHE), followed by a broad oxidation hump (a_2) around 0.55 V, which is visible in the region of the Au oxides [439]. The Au electrode deactivates positive to peak a_2 above 0.65 V, which reveals that Au oxides are relatively inactive towards the BH_4^- oxidation reaction. On the reverse scan, a well defined, sharp, anodic peak (c_1), is observed around 0.3 V, a potential value where it is expected that the Au oxides are reduced and the electrode surface is reactivated. This peak tails off at about 0.15 V, as the potential is scanned into the range where the conversion, $BH_4^- \rightarrow BO_2^-$, is no longer favourable. Peak a_1 is characteristic of an irreversible electrochemical step (E). The other two peaks, a_2 and c_1, correspond also to irreversible electrochemical steps, but deeper analysis of the results suggests that a *CE* or *EC* mechanism is actuating, where *C* denotes coupled chemical reaction (*e.g.*, adsorption). The α coefficients for the purely electrochemical step (E) varied between 0.77 and 0.89, for temperatures ranging from 298 to 338 K, and $NaBH_4$ concentrations between 0.03 and 0.12 M. The number of exchanged electrons, n, for the E step involved less than 8 electrons per BH_4^- anion ($n = 6.8 \pm 0.7$), which is consistent with the proposed [497] overall oxidation process (leading to n between 3 and 8).

8. Sodium borohydride for fuel cells

There are two types of fuel cell systems using $NaBH_4$ aqueous solution as the fuel: the proton exchange membrane fuel cell (PEMFC), which uses H_2 generated *in situ* in a $NaBH_4$ hydrolysis reactor connected to a conventional PEMFC; and the direct borohydride fuel cell (DBFC) system, which also belongs to the PEMFC class, but it is fed directly by a $NaBH_4$ aqueous solution as an anodic fuel.

While the fuel for both these two systems is the same $NaBH_4$ aqueous solution, they have one major difference. In the regular PEMFC, it is necessary to maximise the H_2 generation from the BH_4^- hydrolysis, whereas in the DBFC system, the production of H_2 must be suppressed as much as possible for adequate cell performance.

Accordingly, $NaBH_4$, which was previously known mostly for being a specialty reducing agent in the manufacture of pharmaceuticals and a bleaching agent in the manufacture of paper, is now acquiring increasing importance as an energy/hydrogen carrier. It is an energy carrier when it directly powers a DBFC. It works as a hydrogen carrier when it stores and releases hydrogen that is intended to power a regular PEMFC. In other words, $NaBH_4$ can directly or indirectly power a PEMFC.

8.1. PEMFC systems based on $NaBH_4$

The concept behind this system is based on the PEMFC use of H_2 generated *in situ* via the $NaBH_4$ hydrolysis reaction (Eq. (3)) [253]. As indicated by the stoichiometry of Eq. (3), half of the H_2 produced in the hydrolysis reaction is derived from the solution water, which accounts for the large amount of H_2 generated in this reaction.

$NaBH_4$ solutions rendered basic with NaOH become chemically stabilised and do not generate significant amounts of H_2 under ambient conditions. However, upon the addition of certain heterogeneous catalysts, the $NaBH_4$ hydrolysis rate can be dramatically accelerated. Many conventional catalysts have been proposed for the reaction, of which ruthenium-based catalysts are known to be the most effective for promoting H_2 generation [253].

The H_2 produced in the hydrolysis reactor is then used as the gaseous fuel for the coupled PEMFC, to generate electricity via the general reactions described by Eqs. (21)–(23).

$$H_2 \rightarrow 2H^+ + 2e^- \quad \text{(Anode)} \qquad (21)$$

$$½O_2 + 2H^+ + 2e^- \rightarrow H_2O \quad \text{(Cathode)} \qquad (22)$$

$$H_2 + ½O_2 \rightarrow H_2O \quad \text{(Overall)} \qquad (23)$$

The development of the PEMFC system based on borohydride can be divided into two steps [253]. The first is the development of a hydrolysis mechanism of $NaBH_4$ with a high reaction conversion and a H_2 generation rate sufficient to provide enough fuel for the PEMFC. The second is the establishment of an effective system design for connecting this H_2 supply source to the PEMFC system. The former step is generally accepted as being the key issue. While much research has already been devoted to the H_2 generation via the $NaBH_4$ hydrolysis, it is still somewhat doubtful if the amount of produced H_2 and the reaction rate are sufficiently high to provide the fuel for a PEMFC system. Recently, these technological issues have been partially overcome, both theoretically

and experimentally, by the development of various catalyst systems [232–239]. As a result, the conversion rate of the hydrolysis reaction has been increased to almost 100% at room temperature and the H_2 generation rate has been raised to a level sufficient for a PEMFC. Subsequently, PEMFCs based on borohydride are presently being evaluated by many researchers.

Although most of the research confirms the technological availability of this PEMFC system, in order to $NaBH_4$ be regarded as a promising hydrogen storage material there are some issues that must be solved first [166]. One is the high price of $NaBH_4$ (ca. 50 €kg^{-1}). Another issue is that the hydrolysis reaction does not always follow the ideal route given by the general reaction shown in Eq. (3), but it is rather described by Eq. (24).

$$NaBH_4 + (2+x)H_2O \rightarrow NaBO_2{\cdot}xH_2O + 4H_2 \quad (24)$$

The reaction byproduct is hydrated with x molecules of water, decreasing the gravimetric hydrogen storage capacity from about 11 wt.% to 4–7 wt.%. Attempts should be made to improve these low capacity values. The third issue is the catalyst efficiency, including its reactivity and resistance to deactivation. The performance of the catalysts has received much attention but although their reactivity has been largely studied, little research can be found regarding their resistance. The last issue is the post treatment of the hydrolysis byproducts (anhydrous and hydrated $NaBO_2$). $NaBH_4$ is currently a non-reversible chemical hydride. Hence, a way for recycling $NaBO_2$ into $NaBH_4$ is being investigated, a task with great significance. If $NaBO_2$ cannot be recycled, $NaBH_4$ cannot be regarded as a sustainable or renewable (or rather recyclable) material what will then imply an inevitable problem of boron resources depletion. Furthermore, $NaBO_2$ recycling would greatly contribute to the reduction of the $NaBH_4$ cost up to a projected price of 1 €kg^{-1}. Investigations are in progress [48–51], namely in our Laboratory [51].

8.2. DBFC systems

The direct borohydride fuel cell (DBFC) system uses a $NaBH_4$ aqueous solution as the fuel, which is continuously supplied to the anodic chamber of the fuel cell.

In a DBFC, borohydride, BH_4^-, is oxidised in strong alkaline media (pH >12) to metaborate, BO_2^-, and water, generating eight electrons according to Eq. (20). With the BH_4^- oxidation at the anode, humidified oxygen or air is electrochemically reduced at the interface between the cathode catalyst and the aqueous electrolyte, and the eight electrons are consumed according to Eq. (25)

$$2O_2 + 4H_2O + 8e^- \rightarrow 8OH^- \quad (E^0 = 0.40\,V\ vs.\ SHE) \quad (25)$$

Coupling of Eqs. (20) and (25) leads to the overall cell reaction described by Eq. (26).

$$BH_4^- + 2O_2 \rightarrow BO_2^- + 2H_2O \quad (E^0 = 1.64\,V) \quad (26)$$

The DBFC theoretical cell voltage of 1.64 V is about 0.4 V higher than that of the ordinary PEMFC. It is also very high when compared to the methanol, formic acid, and hydrazine systems, with theoretical cell voltages of 1.19, 1.45 and 1.56 V, respectively.

The performance of fuel cells that operate on $NaBH_4$ as the fuel and oxygen or hydrogen peroxide (H_2O_2) as oxidants has been investigated in several laboratories [253,433,486,515–619]. Although the initial suggestion of using $NaBH_4$ as an anodic fuel dates from 1962 [433], there was a hiatus of almost 40 years until the idea deserved a renewed interest. Fig. 12 shows that over 100 papers on the DBFC have been published since 2003.

The focus of research on the direct borohydride/peroxide fuel cell (DBPFC) is in developing a high energy density power source for space applications, underwater vehicles, and specific terrestrial applications. One of the major advantages of the DBPFC is

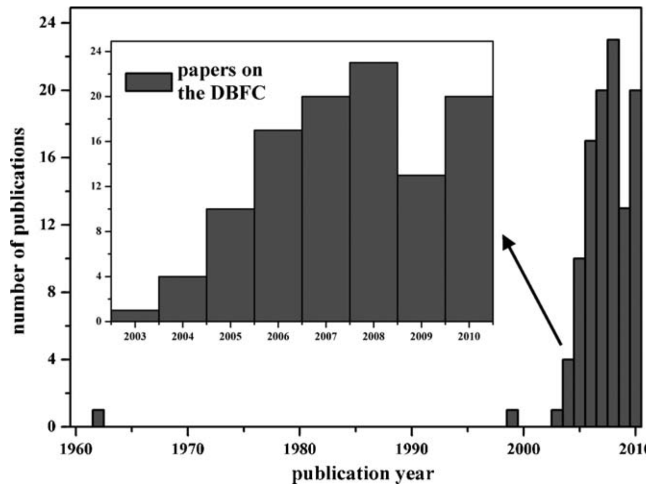


Fig. 12. Evolution of the number of publications concerning the DBFC.

the use of reactants that are liquid at ambient temperature. The use of liquid reactants greatly simplifies the storage, thermal management and internal processing. The minimum energy content of the $NaBH_4/H_2O_2$ reactants is 2600 Wh kg^{-1} (based on total fuel weight), which is comparable to that of H_2/O_2 (3660 Wh kg^{-1}), without the need for cryogenic storage. In addition, high power densities can be achieved in the DBPFC due to the ability of providing a high concentration of reactants to the fuel cell.

In the DBPFC, the BH_4^- anodic oxidation proceeds through Eq. (20) whereas at the cathode H_2O_2 is decomposed into oxygen and water at the catalyst/electrode interface according to Eq. (27), with the produced oxygen being subsequently reduced through Eq. (25).

$$4H_2O_2 \rightarrow 4H_2O + 2O_2 \quad (27)$$

H_2O_2 may also be directly electrochemically reduced according to Eq. (28).

$$4H_2O_2 + 8e^- \rightarrow 8OH^- \quad (E^0 = 0.87\,V\ vs.\ SHE) \quad (28)$$

When the pH of the H_2O_2 catholyte solution is low (pH <1), two reactions may take place: decomposition of H_2O_2 to O_2 (Eq. (27)) followed by O_2 reduction to water (Eq. (29)); or the direct H_2O_2 electroreduction described by Eq. (30).

$$2O_2 + 8H^+ + 8e^- \rightarrow 4H_2O \quad (E^0 = 1.23\,V\ vs.\ SHE) \quad (29)$$

$$4H_2O_2 + 8H^+ + 8e^- \rightarrow 8H_2O \quad (E^0 = 1.77\,V\ vs.\ SHE) \quad (30)$$

Accordingly, the net cell reaction in such an alkaline DBPFC is given by Eq. (31)

$$BH_4^- + 4H_2O_2 \rightarrow BO_2^- + 6H_2O \quad (31)$$

The cell voltages for this DBPFC are 1.64, 2.11, 2.47, and 3.01 V for cathode reactions described by Eqs. (25), (28), (29) and (30), respectively. The cell voltage of 3.01 V is 0.9 V higher than that for H_2O_2 reduction in alkaline solution and assumes the direct electroreduction of H_2O_2 at low pH. Therefore, an appropriate cathode material should promote the reaction shown in Eq. (30), avoiding heterogeneous reactions and surface decomposition to oxygen (Eq. (27)).

Recent studies at our Laboratory have suggested that zinc (Zn) may be a good anode for DBPFCs [209]. A single DBPFC, employing a Zn anode and a Pt cathode, was then assembled and its performance was evaluated [616]. The cell voltage of this DBPFC was lower (2.14 V) than the equilibrium cell voltage, and a stability test showed that the cell was able of stable operation for not more than 6 h. DBPFC discharge curves led to power densities, specific capacities, and energy densities as high as 528 mW cm^{-2},

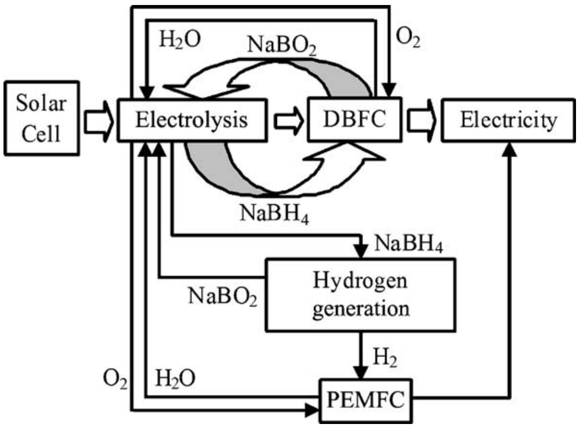


Fig. 13. Sodium borohydride energy system with integrated recharging.

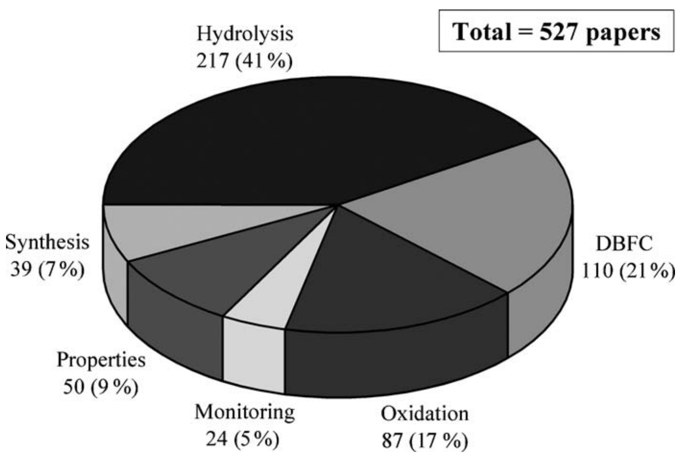


Fig. 14. Division among the number of journal papers devoted to energy-related sodium borohydride research areas.

1577 Ah kg^{-1}, and 2799 Wh kg^{-1}, respectively. A poor rate capability of the cell was demonstrated, being shown that for cell voltages lower than ~1.4 V, the cell may no longer be useful. Polarisation data showed anode limitations (for short-time operation) caused by ohmic losses, particularly at high cell currents. Cathode limitations were only observed for longer operation periods.

It was concluded that to achieve a functional system, several problems need to be overcome. These include the need to alter the Zn anode material (by modification of its metal surface and/or by alloying), to reduce the ohmic losses at the Nafion 117 cation exchange membrane (or testing alternative membrane materials), to chose a more effective electrocatalyst for the direct electrochemical reduction of H_2O_2, to adjust the electrolyte compositions, and to work at temperatures in the range of 313–333 K [495].

Among the remaining challenges to develop practical DBFC systems, a key issue is the inhibition of the $NaBH_4$ crossover. Improvements on the membrane electrode assembly (MEA) or in the liquid diffusion layer, which is more resistant to crossover, could help solving this problem. In addition, an enhancement of the power density of the DBFC should be achieved, which implies a decrease in the effective area of the cell to reduce the $NaBH_4$ crossover.

The development of means of obtaining the complete eight electron reaction, by restraining the BH_4^- hydrolysis, is vital for improving DBFC technologies. Employing electrode materials with high H_2 overpotential and the use of surface treatment technology are considered to be the best way to meet these challenges. In addition, for portable applications, where the cell volume is a critical parameter, it is required a drastic reduction in the volume of the $NaBH_4$ aqueous solution.

9. Conclusions

Apart from its established use for hydriding and reduction processes in the chemical industry, $NaBH_4$ is being, particularly in the present decade, converted to electricity in fuel cells and other energy systems. This is particularly evidenced by specialist journals, like the International Journal of Hydrogen Energy, that are devoting much attention to the subject of $NaBH_4$ as a clean fuel.

$NaBH_4$ can be produced by many ways, as discussed in the present paper, and has many attractive features to generate electricity directly. However, there are many practical engineering and economic considerations that explain why $NaBH_4$ does not already find extensive use as a fuel. A different future in which $NaBH_4$ is produced by electrolytic means seems to be not too much away, and this paper reports some steps towards this direction. Traces of $NaBH_4$ have been detected in the products resulting from electrosynthesis tests in aqueous media and it is suggested that this embryonic study should be pursued. Methods to analyse $NaBH_4$ are described and a newly developed potentiometric technique is suggested for *in situ* monitoring of small $NaBH_4$ concentrations.

The successful utilisation of $NaBH_4$ in energy systems is highly dependent on the reduction of its present price. A substantial decrease in the $NaBH_4$ cost can only be achieved by finding an effective method of recycling $NaBO_2$ back to $NaBH_4$. Of course, if it would be possible to develop a fully reversible system as schematically shown in Fig. 13, interest in $NaBH_4$ would increase exponentially.

The present paper has focused several important aspects concerning the use of $NaBH_4$ for energy systems. Fig. 14 accounts for the total number of papers published on borohydride topics that are relevant for its application in energy systems. Over 300 of these papers have been published very recently, that is, from 2008 onwards, which testify the importance of borohydride as a clean fuel.

Specifically, the uses of $NaBH_4$ as energy carrier for DBFC systems or as hydrogen carrier for conventional PEMFCs have been discussed in detail in this paper. If the problems related to the extent of the $NaBH_4$ crossover, the high cost of the membranes, and the reuse/regeneration of $NaBH_4$, can be overcome, the DBFC option for the renewable energies scenario would be highly enthusiastic. But, as evidenced in Fig. 14, a more promising technology, which may be soon commercialised, is based on the reaction of water and $NaBH_4$ releasing hydrogen that can fuel a fuel cell or be fed into a combustion engine. Following this avenue, it would be possible to develop low cost PEMFCs, without the need for hydrogen storage, and other concerns which may be quickly squelched.

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